

Quasithermodynamics and a Correction to the Stefan–Boltzmann Law

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Abstract

We provide a correction to the Stefan–Boltzmann law and discuss the problem of a phase transition from the superfluid state into the normal state.

Keywords: thermodynamics, Stefan–Boltzmann law, black body, Planck formula, heat emission and absorption, saddle-point method, Landau curve, thermodynamical limit.

In his book [1], Schrödinger notes that the asymptotic form at a large number of particles N can be obtained with a precision not better than \sqrt{N} . The leading term of the asymptotic form as $N \rightarrow \infty$ with the volume $V \rightarrow \infty$ but with $N/V \rightarrow \text{const}$ is called the thermodynamic limit. In the example of the Stefan–Boltzmann radiation law, we show that the next asymptotic term has the order $N^{2/3}$ and that it is impossible to achieve a better precision. We also give this term explicitly. We say that this term, i.e., the limit of the difference between the exact answer and the thermodynamic limit, divided by $N^{2/3}$, is the quasithermodynamic limit.

In this note, we present some general considerations about the thermodynamical limit in statistical physics. First we dwell on the study of the notion of black body.

The Rayleigh–Jeans formula describing black bodies in classical physics, valid for low frequencies, was extended in 1900 to high frequencies in the form of the famous formula due to Planck, who proposed to consider discrete energies and introduced the constant that now bears his name. That formula implies, in particular, the Stefan–Boltzmann formula, which had been discovered earlier.

The derivation of the Rayleigh–Jeans formula is based on the Maxwell equation and the Gibbs distribution in classical mechanics. It also makes use of the complete isotropy of black emission.

On the basis of the assumption that black body emission is completely isotropic (see [2], p.205), we rigorously obtain a correction to the Planck formula and to the Stefan–Boltzmann law. In many precise experiments about black radiation, the necessity of this correction was not noticed. On the other hand, the exact Maxwell equation for free photons, which is used to derive the Rayleigh–Jeans law, does not contain the parameter h , and the appearance of a correction to a law containing this parameter, leads to the problem of carrying over the correction containing the parameter to the Maxwell equation.

As to the Stefan–Boltzmann law, which reads

$$F = -\frac{4\delta}{3c}VT^4, \quad (1)$$

where F is the free energy, V is the volume, c the speed of light, and δ the Stefan–Boltzmann constant, $\delta = \frac{\pi^2 k^4}{60h^4 c^2}$, it is a fact that here small discrepancies between theory and experiment were observed. Thus, the Physical Encyclopedic Dictionary of 1966 [3],

p.82 says: “The experimental value of δ_{exp} is somewhat larger than its theoretical value δ_{theor} obtained by integrating the Planck formula over the wavelength λ (or the frequency ν). The reasons for this discrepancy are not quite clear.”

The quasithermodynamic correction to this law is given by

$$F = -\frac{4\delta}{3c}T^4V - 2\zeta(3)\frac{k^3T^3}{(hc)^2}V^{2/3}, \quad (2)$$

where ζ is the Riemann zeta-function. This result follows from Theorem 3 in [4], pertaining to number theory. This general theorem is applicable to objects in economics, linguistics, and semiotics. In our case, it determines the domain where most of the choices are positioned that satisfy the inequality

$$\sum_{i,j,k}(i+j+k)N_{i,j,k} \leq E, \quad (3)$$

where $E \gg 1$ is fixed, and the $N_{i,j,k}$ are any natural numbers (the number of choices corresponding to (3) is finite). The theorem is roughly formulated as follows (see [5] for the exact formulation): the probability that the number of choices –

$$\left| \sum_{i+j+k \leq s} (i+j+k)N_{i,j,k} - \sum_{i+j+k \leq s} \frac{i+j+k}{e^{(i+j+k)b} - 1} \right| \geq \overline{E}N^{\frac{1}{2}+\varepsilon}, \quad (4)$$

where s is fixed, is exponentially small as $E \rightarrow \infty$; in other words, there are not too many choices outside the specified interval. The parameter b is here determined from the equation

$$\sum \frac{i+j+k}{e^{(i+j+k)b} - 1} = E, \quad (5)$$

and N is the mean value of the sum $\sum_{i,j,k} N_{i,j,k}$ under condition (3), $\overline{E} = E/N$.

This theorem can be applied to quantum statistics if the following assumptions are made:

1. All choices of particle distribution over energy levels are equiprobable (something of the sort of the equidistribution law, which we call the “no-preference law”).

2. Blackbody radiation is totally isotropic.

Suppose we have the condition

$$\sum_{i,j,k}(i+j+k)N_{i,j,k} \leq E, \quad (6)$$

where E is a constant, $N_{i,j,k}$ are “equally chosen” integers, i.e., are equiprobable or equally distributed. Then it follows from the analog of the theorem in [4] that most of the variants will cluster near the following dependance of the “cumulative probability”:

$$B_l = \sum_{i+j+k \leq l}^l N_{i,j,k},$$

with $l \leq s$, $s = \max(1+j+k)$ in inequality (6)

$$B_l = \sum_{i=1}^l \frac{1}{2} \cdot \frac{(i+1)(i+2)}{e^{bi} - 1}, \quad (7)$$

where b is determined from the conditions

$$\sum_{i=1}^s \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1} = E, \quad (8)$$

if $E \rightarrow \infty$. Denote by N the mean value of the sum $\sum_{i,j,k} N_{i,j,k}$ under condition (6).

It turns out that, in this case, most of the variants will also cluster around the following dependance of “local energy”: $E_l = \sum_{i+j+k \leq l} (i+j+k) N_{i,j,k}$, $E_l \leq E$, near

$$\sum_{i=1}^l \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1}, \quad (9)$$

where b is determined from conditions (8) if $E \rightarrow \infty$.

The theorem from [5] can then be stated similarly to the theorem from [4].

Theorem 1 *Suppose that all choices of the families $\{N_i\}$ such that*

$$\sum_{i,j,k} (i+j+k) N_{i,j,k} \leq E, \quad (10)$$

are equiprobable. Then the number of variants \mathcal{N} of families $\{N_{i,j,k}\}$ satisfying (6) and (10) as well as the following additional condition:

$$\left| \sum_{i+j+k \leq l} (i+j+k) N_{i,j,k} - \sum_{i=1}^l \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1} \right| \geq \bar{E} N^{1/2} (\ln N)^{1/2+\varepsilon}, \quad (11)$$

is less than $(c_1 \mathcal{N}) / \mathcal{N}^\dagger$, where c_1 and m are arbitrary numbers); here $\bar{E} = E/N \sim 1/b$.

Notation: \mathcal{M} is the set of all families $\{N_{i,j,k}\}$ satisfying condition (6), $\mathcal{N}\{\mathcal{M}\}$ is the number of elements of \mathcal{M} , \mathcal{A} is a subset of \mathcal{M} satisfying the condition

$$\left| E_l - \sum_{i=0}^l \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1} \right| \leq \Delta, \quad l = 0, 1, \dots, s,$$

where Δ and b are some real numbers not depending on l .

Denote

$$\left| E_l - \sum_{i=1}^l \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1} \right| = S_l.$$

Let us recall the scheme of the proof, similar to that of Theorem 3 from [4], in our case.

It is obvious that if \mathcal{M} is the number of families $\{N_{i,j,k}\}$, then

$$\mathcal{N}\{\mathcal{M} \setminus \mathcal{A}\} = \sum_{\{N_{i,j,k}\}} \left(\Theta \left\{ E - \sum_{i,j,k} (i+j+k) N_{i,j,k} \right\} \delta_{(\sum_{i,j,k} (i+j+k) N_{i,j,k}), N} \prod_{l=0}^s \Theta \left\{ |S_l - \Delta| \right\} \right). \quad (12)$$

Here the sum is taken over all integers $N_{i,j,k}$, $\Theta(\lambda)$ is the Heaviside function, and δ_{k_1, k_2} is the Kronecker delta.

Using the integral representations

$$\delta_{NN'} = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\varphi e^{-iN\varphi} e^{iN'\varphi}, \quad (13)$$

$$\Theta(y) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\lambda \frac{1}{\lambda - i} e^{by(1+i\lambda)}. \quad (14)$$

and performing the standard regularization, we obtain

$$\int_0^{\infty} dE \Theta\left(E - \sum_{i,j,k} (i+j+k)N_{i,j,k}\right) e^{-bE} = \frac{e^{-b \sum_{i,j,k} (i+j+k)N_{i,j,k}}}{b}. \quad (15)$$

Denote

$$Z(b, N) = \sum_{\{N_{i,j,k}\}} e^{-b \sum_{i,j,k} (i+j+k)N_{i,j,k}},$$

where the sum is taken over all $N_{i,j,k}$. Further, introduce the notation

$$\zeta_l(i\alpha, b) = \prod_{i=1}^l \xi_i(i\alpha, b), \quad \xi_j(i\alpha, b) = \frac{1}{(1 - e^{i\alpha - bj})^{j(j+1)/2}}, \quad j = 1, \dots, l.$$

It follows from (13) that

$$Z(b, N) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\alpha e^{-iN\alpha} \zeta_s(i\alpha, b); \quad (16)$$

hence

$$\begin{aligned} \mathcal{N}\{\mathcal{M} \setminus \mathcal{A}\} &\leq \left| \frac{e^{bE}}{i(2\pi)^2} \int_{-\pi}^{\pi} \left[\exp(-iN\varphi) \right. \right. \\ &\quad \times \sum_{\{N_{i,j,k}\}} \left(\exp\left\{ \left(-b \sum_{i,j,k} (i+j+k)N_{i,j,k} \right) + (i\varphi)N_{i,j,k} \right\} \right) \left. \right] d\varphi \\ &\quad \times \prod_{l=0}^s \Theta(|S_l - \Delta|) \Big|, \end{aligned} \quad (17)$$

where b is a real parameter for which the series converges.

Estimating the right-hand side, carrying the absolute value sign under the integral and then further under the sum, we obtain after integration over φ

$$\begin{aligned} \mathcal{N}\{\mathcal{M} \setminus \mathcal{A}\} &\leq \frac{e^{bE}}{2\pi} \sum_{\{N_{i,j,k}\}} \exp\left\{ -b \sum_{i,j,k} (i+j+k)N_{i,j,k} \right\} \times \\ &\quad \times \prod_{l=0}^s \Theta(|S_l - \Delta|). \end{aligned} \quad (18)$$

From the inequality for the hyperbolic cosine $\cosh(x) = (e^x + e^{-x})/2$

$$2^s \prod_{l=0}^s \cosh(x_l) \geq e^{\delta} \quad \forall x_l: \sum_{l=0}^s |x_l| \geq \delta \geq 0, \quad (19)$$

it follows that, for all positive c and Δ , we can write (compare [6], [7])

$$\prod_{l=0}^s \Theta(|S_l - \Delta|) \leq 2^s e^{-c\Delta} \prod_{l=0}^s \cosh\left(c \sum_{i+j+k \leq l} (i+j+k) N_{i,j,k} - c\psi_b\right), \quad (20)$$

where

$$\psi_b = \sum_{i=1}^l \frac{1}{2} \cdot \frac{i(i+1)(i+2)}{e^{bi} - 1}.$$

Thus, we obtain

$$\begin{aligned} \mathcal{N}\{\mathcal{M} \setminus \mathcal{A}\} &\leq e^{-c\Delta} \exp(bE) \sum_{\{N_{i,j,k}\}} \exp\left\{-b \sum_{i,j,k} (i+j+k) N_{i,j,k}\right\} \\ &\quad \times \prod_{l=0}^s \cosh\left(\sum_{i+j+k \leq l} c(i+j+k) N_{i,j,k} - c\psi_b\right) \\ &= e^{bE} e^{-c\Delta} \prod_{l=0}^s \{\zeta_l(0, b-c) \exp(-c\psi_b) + \zeta_l(0, b+c) \exp(c\psi_b)\}. \end{aligned} \quad (21)$$

Let us apply Taylor's formula to $\zeta_l(0, b \pm c)$. There exists a $\gamma < 1$ such that

$$\ln(\zeta_l(0, b \pm c)) = \ln \zeta_l(0, b) \pm c(\ln \zeta_l)'_b(0, b) + \frac{c^2}{2} (\ln \zeta_l)''_b(0, b \pm \gamma c).$$

Obviously,

$$\frac{\partial}{\partial b} \ln \zeta_l \equiv -\psi_b.$$

Let us put $c = \Delta/D(0, b)$, where $D(0, b) = (\ln \zeta_l)''_b(0, b)$ is positive for all b and monotonically decreases as b increases. The right-hand side of (21) does not exceed

$$2^\gamma e^{bE} \prod_{p=0}^s \zeta_{l_p}(0, b) e^{-(\Delta_l^2)/|D(0,b)|} + \frac{\Delta_l^2 D(0, b - \gamma \Delta/D(0, b))}{2(D(0, b))^2}.$$

As in [4], we obtain

$$\mathcal{N}(\mathcal{M} \setminus \mathcal{A}) \leq e^{bE} \zeta_l(0, b) e^{-\varepsilon \Delta^2/D(0,b)}. \quad (22)$$

Therefore, in the interval from $-\pi$ to π over which the integral (16) is taken, the only contribution comes from a neighborhood of the point $\alpha = 0$. Let us compute the integral (16) by the Laplace method with precision up to N^{-m} and then apply all the subsequent arguments from the proof of Theorem 3 in [4].

In order to estimate $\zeta_s(0, \beta)$ from below, we can use the exact asymptotics obtained by Krutkov [8] for the three-dimensional oscillator. In the case of a general spectrum λ_n , the formula obtained by the saddle-point method meets with considerable difficulties due to the fact that an infinite number of saddle points can appear in certain concrete examples (Koval', private communication).

Note that the sum over all variants satisfying inequality (6) may be interpreted as a discrete continual "path integral", the paths being the variants. The asymptotic leading term of the continual integral is concentrated, as a rule, near one principal "trajectory"

(this is the Laplace method for the continual integral), and rapidly tends to zero outside a neighborhood of this trajectory. This is expressed by the statement of the theorem. The size of this neighborhood (in our case $\overline{EO}(N^{1/2}(\ln N)^{1/2+\varepsilon})$) determines the limiting precision with which it makes sense to compute this “principal trajectory”.

In this connection, we propose the following somewhat modified conjecture about the Schrödinger rule that he qualified as a “law of nature”. If a certain number of particles, molecules, genes in a chromosome is equal to N , then one can obtain a statistical law with precision of no more than $O(\sqrt{N \ln N})$. The mathematical meaning of this conjecture is that estimate (11) cannot be improved by more than ε .

Since $E \rightarrow \infty$ in (8), it follows that we can put $s = \infty$ in the sum

$$\sum_{i=1}^{\infty} \frac{i(i+1)(i+2)}{2(e^{bi} - 1)},$$

we can apply the Euler formula of the form

$$\begin{aligned} \sum_{b > n > a} f(n) &= \int_a^b f(x) dx + \rho(b)f(b) - \rho(a)f(a) \\ &\quad + \sigma(a)f'(a) - \sigma(b)f'(b) + \int_a^b \sigma(x)f''(x) dx \\ \rho(x) &= \frac{1}{2} - \{x\}, \quad \sigma(x) = \int_0^x \rho(t) dt. \end{aligned} \tag{23}$$

Since $\sigma(x) \leq 1/8$, it is easy to see that

$$E = \frac{\zeta(4)}{12} b^{-4} + \frac{3}{4} \zeta(3) b^{-3} + O(b^{-2}),$$

where $\zeta(x)$ is the Riemann zeta function. Therefore, $b \rightarrow \infty$. As is known, $\zeta(4) = \pi^4/90$.

Similarly, in the right-hand side of (11), we can pass to integrals for sufficiently large values of l .

In view of (11), the term $O(b^3)$ is greater than $\overline{E}\sqrt{N \ln N}$ and its calculation makes no sense.

Similar estimates for N , as can be seen from Theorem 1 from [5], also make possible the computation of the asymptotic (in b) terms $O(b^{-3})$ and $O(b^{-2})$ only. The leading (first) term of the asymptotics will be called the *thermodynamical limit* and the second one, the *quasithermodynamical limit*.

Now let us consider a system of N three-dimensional noninteracting oscillators of the same frequency ω_0 :

$$-\frac{\hbar^2}{2m} \Delta \Psi_n(x) - \omega_0^2 |x|^2 \Psi_n(x) = n \Psi_n(x), \quad x \in \mathbb{R}^3. \tag{24}$$

In order to obtain the leading term of the Stefan–Boltzmann law for this system of oscillators, we must set

$$b = \frac{\omega_0 \hbar}{kT};$$

here \hbar is the Planck constant, k is the Boltzmann constant, T the temperature, ω_0 the frequency, which equals $\omega_0 = c/\sqrt[3]{V}$, where c is the speed of light, and V is the volume. We assume that the oscillators are completely isotropic, so that the frequency ω_0 is the

same in all directions. Oscillations of frequency ω greater than ω_0 do not exist at the given temperature, while the frequencies $\omega < \omega_0$ give a considerably lesser number of variants and may be neglected.

As a result, for the correction to the Stefan–Boltzmann law, we obtain a quasithermodynamical term of the form

$$F = -\frac{4\delta}{3c}T^4V - \frac{12\hbar\delta}{k} \cdot \frac{\zeta(3)}{\zeta(4)}T^3V^{2/3}, \quad (25)$$

where F is the free energy, $\delta = \pi^2k^4/(60\hbar^3c^2)$ is the Stefan–Boltzmann constant, V is the volume, c , the speed of light, \hbar is the Planck constant, k is the Boltzmann constant, and T is the temperature.

It has *always* been observed that the experimental values of the Stefan–Boltzmann constant are larger than their theoretical values. Now the reason for this discrepancy is clear: the correction term specified above explains this discrepancy.

However, the main effect of quasithermodynamics occurs when there is no thermodynamical phase transfer, but there is a quasithermodynamical one. It is precisely such an effect that was obtained by the author in the study of a Fermi-gas without the additional assumption on the existence of Cooper pairs. It was assumed that the number of particles N tends to ∞ , the particle interaction is pairwise, as in Helium 4, i.e, repulsive at short distances and attractive at large ones. At the same time, the potential $V(r_i - r_j)$ is mainly a short distance one. The corresponding spectrum has the form

$$E_l = \frac{\hbar^2 l^2}{2m} + \tilde{V}(l) - \tilde{V}(0), \quad (26)$$

where $\tilde{V}(l)$ is the Fourier transform of $V(z)$.

As N tends to infinity and the volume V tends to infinity in such a way that $N/V \rightarrow \text{const}$, the potential tends to the δ -function and therefore tends to the spectrum of an ideal gas. Superfluidity arises only in the quasithermodynamical limit. In this limit, as a rule, the Landau curve arises. Thus, the phase transfer to the superfluid state occurs in the quasithermodynamics of this “model”. Note that this model does not contain any additional physical interactions: it is a “model without a model”, since the antisymmetric solution of the N -particle Schrödinger equation with the ordinary pairwise interaction cannot be regarded as a “model”. This is an ordinary mathematical problem.

Let us consider a Bose-gas. Bogolyubov proposed the following spectrum in this case:

$$E_l = \sqrt{\left(\frac{\hbar^2 l^2}{2m} + \tilde{V}(l)\right)^2 - \tilde{V}(l)^2}, \quad (27)$$

which also yields the Landau curve in quasithermodynamics. But unlike (26), in the thermodynamical limit it gives

$$\lim_{N/V \rightarrow \text{const}, N \rightarrow \infty} E_l = \sqrt{\left(\frac{\hbar^2 l^2}{2m} + \tilde{V}(0)\right)^2 - \tilde{V}(0)^2},$$

and superfluidity is preserved (the critical Landau speed in the thermodynamical limit is not zero, as it is in the case of the spectrum (26)). However, the photon part of the spectrum disappears in the thermodynamical limit and appears only in quasithermodynamics.

Remark. Bogolyubov's work may be rigorously founded under certain additional conditions, provided one considers the problem, as Bogolyubov did, on the three-dimensional torus. However, the passage to the limit from the torus to three-dimensional space is erroneous: an everywhere dense point spectrum appears in the limit.

The author obtained a modification of formula (27) for the case in which the liquid flows through a capillary of radius r . The spectrum in that case has the form

$$\begin{aligned}
E_l = & \left[\frac{1}{2} \left(a(l^2 - k_2^2) + \frac{\tilde{V}(l - k_2) - \tilde{V}(k_2)}{2} \right)^2 + \frac{1}{2} \left(a(l_1^2 - k_2^2) + \frac{\tilde{V}(l - k_2) - \tilde{V}(k_2)}{2} \right)^2 \right. \\
& + \left(\frac{\tilde{V}(l + k_2) + \tilde{V}(k_2)}{2} \right)^2 - \left(\frac{\tilde{V}(l - k_2) + \tilde{V}(l + k_2)}{2} \right)^2 \\
& + \frac{1}{2} (a(l_1^2 + l^2 - 2k_2^2) + \tilde{V}(l - k_2) - \tilde{V}(k_2)) \\
& \left. \times \sqrt{a^2(l_1^2 - l^2)^2 + 2(\tilde{V}(l + k_2) + \tilde{V}(k_2))^2} \right]^{1/2},
\end{aligned} \tag{28}$$

where

$$a = \frac{h^2}{2m}, \quad l_1 = l + 2k_2,$$

while $k_2 = 2\pi n/r$, where $n = 1, 2, \dots$.

When $r = \infty$, and hence $k_2 = 0$, we obtain the Bogolyubov formula (27). In the limit as $r \rightarrow 0$, $k_2 \rightarrow \infty$, $l = (l_0, -k_2)$ (l_0 is the component along the direction of flow), we obtain

$$\lim_{r \rightarrow 0} E_{l_0} = \sqrt{a^2 l_0^4 + a |\tilde{V}(l_0)| l_0^2}.$$

These results, just as the Bogolyubov formula, are valid in the thermodynamical limit with the quasithermodynamical correction.

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